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(54) Oxidation catalysts and their production

(57) Redox catalysts comprise copper chemically bonded to the support. They may include divalent palladium as a redox couple for the copper which should be mainly divalent. The copper on surfaces of the catalyst may be substantially monovalent. They may be made by evaporating to dryness onto a support containing the copper a solution providing the redox couple. The support containing copper may be made by ion exchange. Activation is achieved by heating for half to 4 hours, preferably in the presence of moisture vapour at the end of the heating. The catalysts can be used in smoking products or filters for the oxidation of carbon monoxide.

GB 2042364 A

SPECIFICATION

Catalysts and their production

- 5 It is well known that redox catalysts can be formed comprising a support carrying two redox components, one being copper and the other being a redox couple for copper. One of the components serves as a catalyst for the reaction that is to be catalysed while the other serves to return the catalytic component to its original state. For instance an accepted mechanism for the catalytic oxidation of hydrocarbons with such a catalyst in which the redox couple is palladium
- 10 assumes that divalent palladium oxidises the hydrocarbon and is reduced to zerovalent palladium, divalent copper oxidises the zerovalent palladium back to divalent palladium and forms monovalent copper, and monovalent copper is oxidised by oxygen back to divalent copper, the reactions requiring the presence of water and oxygen.
- Known methods of making redox catalysts containing copper and a redox couple often
- 15 comprise impregnating the support with a solution containing compounds providing copper and palladium or other redox components and evaporating the impregnated support to dryness. It has also been proposed to carry out the impregnation in two stages, with one of the redox components being applied before the other. After deposition the support may be calcined to convert the redox components to the oxide or metal form. Typical disclosures are US Patent
- 20 Specification No. 3,300,528 and British Patent Specification No. 1,438,557. As is apparent from those disclosures various supports may be used, activated carbon often being the support and being shown in Table IV of Specification 1,438,557 to give the most active catalyst compared to, for instance, an alumino silicate.
- According to a first aspect of the invention a catalyst comprises a support, copper chemically
- 25 bonded to the support, and a minor amount of a redox couple for the copper. A process according to the invention for making a redox catalyst comprises forming a catalytic support to which copper is chemically bonded and then depositing a minor amount of a redox couple onto the support.
- It is essential to the invention that a substantial part at least of the copper is chemically
- 30 bonded to the support as opposed to being merely adsorbed onto the support as an adsorbed copper salt, e.g. copper chloride. It is therefore essential that the support contains sites at which bonding of copper can occur. The bonding generally is mainly electrovalent. The support can be formed initially with ionically bonded copper in it, for instance by precipitation of aluminium hydroxide gel from an alkaline liquor containing a copper salt followed by drying the gel, but
- 35 generally the copper is ionically bonded into the support as a result of ion exchange. Accordingly the support must be one that is capable of undergoing ion exchange. Supports such as activated carbon or normal silica can be used but are less satisfactory than supports containing a greater number of ion exchange sites. The support may be alumina but preferably is an alumino silicate, most preferably a zeolite. Preferably it has a pore size of 30 Angstroms or less, generally 4 to 16 Angstroms, with zeolite 13X being very satisfactory.
- 40 Simply saturating the support with an aqueous copper salt solution followed by evaporation to dryness in the normal manner usually does not result in satisfactory ion exchange of copper into the support since the amount of ion exchange copper will be low, the support may include substantial amounts of copper compound that is not chemically bonded to the support and the
- 45 support may also carry the ions that the copper should have replaced. Preferably the support is impregnated with a solution of a copper salt, ion exchange is permitted to occur, excess solution is removed and the impregnation is then repeated at least once and usually more, e.g. 3 to 6 times. Finally the catalyst is washed and dried. The copper salt solution should not be too concentrated as otherwise the activity may be impaired, the concentration generally being below
- 50 50 grams per litre, preferably 20 to 40 grams per litre. The solvent is generally water. Since the anion of the copper salt is removed together with the cation that is being replaced and the excess solution the particular salt is not critical, but the nitrate or chloride is generally preferred.
- By this technique, it is ensured that most, and often all, the copper is chemically bonded to the support and even though, as mentioned below, cupric chloride can subsequently be added
- 55 by a conventional impregnation and dehydration technique the amount is always relatively low compared to the amount of copper that is bonded to the support. At least 50% by weight of the copper on the support, usually at least 70% and preferably at least 90%, is bonded to the support.
- The activity of the final catalyst is inferior if the amount of ionically bonded copper is low, and
- 60 in particular if it is significantly below the maximum amount that can be ion exchanged into the support. Preferably the support is chemically substantially saturated with such copper, for instance containing at least 50% and preferably at least 75% of the maximum amount that can be ionically exchanged into the support.
- Before conducting the ion exchange with the copper solution, the support may have its
- 65 balancing cations exchanged with lithium or other ions.

Any compound capable of serving as a redox couple with copper may be used in the invention. It may consist of a single compound or of a mixture of compounds in which event it is sometimes convenient to look upon one compound of the mixture as the redox couple and another compound of the mixture as a promoter for the redox couple.

- 5 The redox couple is generally an inorganic compound and this compound and any promoter 5
for it are generally in the form of an acetate or, preferably, a chloride. Suitable promoters include stannic and calcium compounds but lithium compounds are preferred. Cupric compounds may also be used as promoter. It is possible that the promotion effect (i.e. improvement in activity) is caused partly and perhaps mainly by the anion, which is preferably chloride, that is 10
10 introduced with the cation. 10

Suitable inorganic compounds as redox couples are noble metal compounds including iridium, ruthenium or rhodium compounds, generally the trichloride, or palladium compounds. Preferred redox couples include divalent palladium, i.e. Pd^{2+} . Preferably it is a chloride, generally being introduced onto the support as PdCl_4^{2-} .

- 15 The inclusion of compounds of cerium and/or manganese in the catalyst is often beneficial. 15
The deposition of the redox couple or promoter is best effected by impregnating the support with a solution of the redox couple or promoter and evaporating to dryness. The redox couple and promoter can be impregnated in succession in either order but preferably the redox couple and any promoter that is to be introduced are impregnated together from a solution containing 20
20 both and the support is then evaporated to dryness. This method results in anions in the solution remaining in the support. The solution may be in any suitable solvent, preferably substantially non-aqueous. Methanol and dichloromethane are particularly suitable and may be used as a mixture. 20

- The concentration of the redox couple in the solution is generally below 2%, for instance 25
25 0.001 to 1% preferably 0.005 to 0.1%, by weight measured as metal, e.g. palladium. The concentration of promoter, measured as metal, in this solution or any other impregnation solution used in the invention is generally within the same range. 25

- The catalysts of the invention generally comprise from 1 to 10% of chemically bonded copper and a much smaller amount, generally less than 20% by weight based on the weight of copper, 30
30 of the redox couple, the amount of redox couple being measured as metal when the couple is an inorganic compound. For instance the amount of palladium or other metallic component of redox couple may be from 0.1 or 1% up to 20%, preferably 5 to 20%, based on the weight of copper. Preferred catalysts comprise 2 to 7%, most preferably 3 to 6%, by weight chemically bonded copper and 0.05 to 2%, preferably 0.1 to 0.5% by weight metal of palladium 35
35 compound or other redox couple. When promoters are included, the amount is generally from 0.5 to 2.5 parts by weight per part by weight of the redox couple, all amounts being measured as metal. Preferably the amount of promoter is about 1 part by weight or sometimes up to 2 parts by weight when the promoter is monovalent, for instance lithium, with double these amounts for higher valent promoters such as calcium. 35

- 40 A preferred process according to the invention comprises impregnating zeolite with an aqueous copper salt solution, permitting ion exchange to occur, removing the excess solution and repeating the impregnation at least twice, preferably then washing and drying the support, impregnating the support with a solution providing 0.1 to 0.5%, measured as metal and based on the weight of catalyst, PdCl_4^{2-} and a substantially equal amount lithium chloride or up to 45
45 twice the amount of calcium chloride or stannic chloride, and evaporating the catalyst to dryness. 45

- The catalyst should be used without any of the chemical after treatments normally used in the prior art, e.g. high temperature reduction. However we have found that the activity of the catalyst can be increased greatly by subsequently heating it under moderate conditions, namely 50
50 100 to 200°C preferably for half to 4 hours. Lower temperatures do not seem to increase activity and higher temperatures tend to damage the catalyst. The temperature is preferably at least 120°C and preferably the heating is conducted for from 1 to 3 hours at about 150°C. 50

- Particular improvement in activity is obtained if the catalyst is contacted with water vapour for at least 15 or 30 seconds at the specified temperature at the end of the heating. The contact 55
55 with water vapour is generally for at least 5 minutes, usually at least 10 minutes but it is generally unnecessary for the contact to be longer than 20 minutes. 55

A convenient way of carrying out the activation is to conduct most of the heating under vacuum in a closed vessel and then to introduce sufficient water vapour to raise the pressure to atmospheric and complete the heating in this atmosphere.

- 60 Instead of activating by heating in the presence of steam activation may also be achieved by exposing the catalyst resulting from substantially dry heating to atmospheric moisture for 1 to 2 days or activation may be completed during use of the catalyst. For instance it may be heated immediately prior to use. The catalyst generally has a blue colour. The contact with moisture may reduce the colour intensity of the catalyst and as soon as this has been observed the 65
65 contact with water vapour can be terminated. The amount of water vapour absorbed for 65

optimum activation is generally at least 10 mg per gram catalyst. Preferably the amount is at least 25 mg, most preferably 50 to 100 mg, per gram catalyst. Amounts above 200 mg per gram are usually unnecessary.

It is well known that some redox catalysts containing copper will contain copper mainly in the divalent state but that some of the copper will pass through a transient monovalent stage during the catalytic process.

According to a second aspect of the invention, we have now surprisingly found that, instead of merely permitting monovalent copper to be formed as a transient intermediate during use, improved results are obtained if a stable redox catalyst is formed which is a product comprising a support carrying divalent copper, the exposed surface of the deposit comprising substantially monovalent copper. By saying that the catalyst is stable we mean that it is preformed, before use in the desired catalytic process, and is capable of being stored for, significant periods of time, for instance many hours or days or weeks, before use, for instance in an impermeable packet.

The substantially monovalent copper on the surface is in intimate contact with divalent copper, which forms a substrate for the substantially monovalent copper. Preferably substantially all the copper on the surface is in substantially monovalent form since although some divalent copper can be tolerated it tends to reduce the activity of the catalyst. The amount of monovalent copper should be low, compared to the amount of divalent copper, and may be provided by, for instance, a monomolecular layer. The amount should not be more than the amount required to form a layer a few molecules thick on the divalent copper.

The presence of bivalent copper in the catalyst can be observed by electron spin resonance measurements (ESR). The valency state of the copper in the surfaces can be determined by electron spectroscopy chemical analysis (ESCA). By referring to the surface comprising substantially monovalent copper we mean that the copper is in a valency state lower than divalent copper but substantially above zerovalent, as determined by ESCA, and preferably has an electron binding energy substantially equivalent to that of monovalent copper although it may have a valency state slightly higher, for instance about 1.2. Preferably the surface, as determined by ESCA, is substantially free of divalent copper. The analysis may be by, for example, a Vacuum Generators E.S.C.A. 3 Spectrometer in which the base pressure of the analyser chamber is 1×10^{-8} Torr and of the sample chamber is 1×10^{-7} Torr. Observation of the Cu2p doublet shows the binding energy for Cu2p_{3/2}. Divalent copper (CuO) has a binding energy of about 933.6 eV. In the invention the binding energy is preferably between 932.2 and 933.4, most preferably 932.5 to 933.3.

The copper containing deposit in the catalyst may be physically adsorbed onto the support but is preferably bonded to the support e.g. as described above. Preferably the catalyst includes also a redox couple for copper, this redox couple generally being present as a minor amount compared to the amount of copper. Preferably therefore the catalyst which has substantially monovalent copper on its exposed surfaces is a catalyst made from the materials and by the methods described in detail above. The activation by heating, especially in the presence of moisture vapour, appears to result in the formation of substantially monovalent copper. Broadly the monovalent copper catalysts are best made by heating a catalyst comprising a support carrying a deposit comprising divalent copper under conditions such as to convert the exposed surface of the deposit to monovalent copper compound, preferably while leaving the underlying copper in the divalent state.

To promote the formation of substantially monovalent copper the catalyst may be reduced during or after its formation. For instance a reducing agent such as stannous tin, cerium as Ce^{3+} or thallium Tl^{1+} may be deposited before the redox couple. The amount of reducing agent is generally very small, e.g. 0.01 to 10%, usually 0.5 to 2% measured as metal by weight of copper. It may be ion exchanged onto the support with the copper or after the copper or may be deposited onto the copper by evaporation of a solution containing the reducing agent, generally before depositing the redox couple and any promoter for the redox couple.

Instead of or in addition to producing monovalent copper by activation, e.g. with steam as described above, and/or by including an inorganic reducing agent, the divalent copper can be reduced by a gaseous reducing agent, for instance carbon monoxide. This is generally effected before the deposition of any redox couple and promoter.

All the catalysts described above are of value in any environment where a redox catalyst may be used, e.g. in the oxidation of olefines (for instance in the production of vinyl acetate), production of vinyl chloride, pollution control (for instance in an automobile exhaust), production of hydrogen by water gas reaction and carbon monoxide oxidation. They can be very satisfactory in the low temperature catalytic oxidation of carbon monoxide to carbon dioxide, with the result the catalysts according to the invention are of particular value for incorporation in smoking products or filters for smoking products. Thus they may be used as the catalytic component of the smoking products or filters as described in British Patent Specification No. 2014376.

The catalysts are normally in powder form, e.g. below 1 mm. They are active in the presence

of water at room temperature, are not seriously deactivated by tars, and substantially maintain activity when used discontinuously, e.g. when a cigarette is puffed. They may be included in smoking products but preferably they are included in the filter of a smoking product. The filter may be a triple filter with catalytic powder, either by itself or mixed with adsorbents such as granular carbon, in a central component between fibrous end portions. The powder may be loose or may be bonded into a porous plug. The powder especially if it has a particle size of below 50 microns, e.g. 5 microns, may alternatively be bonded to fibres that form the central portion of a triple filter or that are distributed throughout some or all of any filter construction or the catalytic powder may be bonded to a sheet which is crumpled or spirally wound to form part or all of the filter. The amount of catalytic powder need only be sufficient to cause catalytic oxidation. Thus, for instance, a filter for a typical smoking product may contain less than 1 mg catalyst, measured by weight of palladium, normally about 0.01 to 0.5 mg catalyst, measured as weight of palladium.

The following Examples illustrate various aspects of the invention.

Example 1

Zeolite 13X was immersed in an aqueous solution of 30 g/l cupric nitrate, left to soak in that solution to permit ion exchange to occur and was then separated from the remaining solution. The separated product was then immersed in fresh solution and the whole process repeated until it has been given three immersions. Analysis showed at the time that the catalyst contained from 3 to 6% copper based on the dry weight. The product was then washed with water and dried. It was then immersed in sufficient of a solution of Na_2PdCl_4 in equal parts methanol and methylene dichloride to provide 0.5% Pd, measured as metal, in the catalyst, and the product dried at room temperature. A typical solution contains 7.5 mg Pd, as Na_2PdCl_4 , in 100 ml solvent. Different samples of this catalyst were then heated in air for two hours at various temperatures and their activity determined.

In this and other examples catalyst activity is expressed as the percentage of CO removed from a standard gas mixture containing 13% O_2 , 10% CO_2 , 3% CO and the balance nitrogen, when the mixture is puffed ten times through 500 mg of the catalyst under standard smoking conditions i.e. 1 puff per minute of 35 ml volume and 2 seconds duration. All 10 puffs are combined and the CO reduction determined. More than one 10 puff cycle can be used.

The results obtained are as follows:

Temperature °C	25	100	150	200	250	300
Activity	20	52	76	66	41	31

From this it will be seen that optimum activity was obtained at 150°C.

Example 2

The process of Example 1 was repeated using various palladium concentrations and with the incorporation of various promoters in the palladium solution and the catalyst content of palladium and promoters was as follows

	Catalyst	
A	13X Cu/0.25% Pd as PdCl_2	
B	13X Cu/0.25% Pd as PdCl_2	+ 0.25% Li^+ as LiCl
C	13X Cu/0.25% Pd as PdCl_2	+ 0.5% Sn^{4+} as SnCl_4
D	13X Cu/0.25% Pd as PdCl_2	+ 0.5% Cu^{2+} as CuCl_2
E	13X Cu/0.1% Pd as PdCl_2	
F	13X Cu/0.1% Pd as PdCl_2	+ 0.25% Li^+ as LiCl
G	13X Cu 0.1% Pd as PdCl_2	+ 0.5% Sn^{4+} as SnCl_4

When the activity of these catalysts was determined against a standard gas mixture as in Example 1 in a series of 10 puff experiments, catalysts A and E has the lowest activity and all the catalysts containing promoters had higher and longer lasting activity. Catalysts B and D were particularly satisfactory.

Example 3

The process of Example 1 was repeated and samples of the resultant catalyst were subjected to different treatments after the heating and the activity determined. It was found that activity increased upon storage in a stoppered bottle but increased more if it was exposed to the atmosphere for 24 hours after the heating. The best increase in activity was caused by including

steam in the atmosphere towards the end of the heating.

Example 4

Zeolite molecular sieve, type 13X, was ion exchanged in triplicate with 3% aqueous cupric nitrate, washed with distilled water and dried in air at about 35°C. A solution containing Na_2PdCl_4 and LiCl in 50/50 methanol/methylene chloride (or methanol alone) was applied and allowed to evaporate leaving a free flowing powder having Pd and Li loadings of between 0.1% and 0.5%. 5

The catalyst was activated by first heating in a bottle for $1\frac{1}{2}$ hours at 150°C after which time a small sample tube is introduced and the bottle sealed with a rubber septum. Water at the rate of from 50 to 100 mg/g of catalyst was added through the septum via a syringe into the empty tube, where it evaporated. The contents were maintained at 150°C for a further 15 minutes. The resultant catalyst had good activity, especially when included in a smoking product filter in an amount such as to give 0.25 mg palladium in the filter. 10

Better results could be obtained when the activation was conducted by heating the catalyst in a closed tube while applying vacuum to about 1 millimetre mercury for the desired period and then introducing water into the vessel, while under vacuum, and then heating the water, the temperature and the amount of water being such that the pressure in the vessel is substantially 1 atmosphere, due substantially entirely to the water vapour in the vessel. 15

Electron spin resonance examination of the catalyst before the heating steps showed that the catalyst contained divalent copper and ESCA determination at this stage showed that there was substantially no monovalent copper present on the surface. ESCA determination of the catalyst that had been activated by heating and steaming at 150°C showed that the surface consisted substantially only of substantially monovalent copper, the recorded binding energy for $\text{Cu}2\text{P}_{3/2}$ being 933.25. ESCA showed no significant trace of divalent copper, but ESR showed the presence of divalent copper. 20 25

Example 5

The process of Example 1 was repeated, but using 0.25% Na_2PdCl_4 measured as metal and with various amounts of LiCl or CaCl_2 as promoter. With calcium chloride the highest activity (about 90) was obtained when the amount was 0.5% by weight, measured as calcium. When the promoter was lithium chloride, the highest activity (about 93) was obtained when the amount was 0.25% by weight measured as lithium, but good activity (about 90) was also obtained when the amount was 0.5%. When the amount was 0.1% the activity was about 75 and when the amount was 1% the activity was about 40. 30 35

Example 6

The process of Example 1 was repeated but modified by contacting the ion exchanged zeolite with a solution containing stannous chloride before contact with the palladium solution. The stannous chloride solution was evaporated to dryness. The amount of stannous chloride was about 1% based on the amount of copper in the support. Similar results could be obtained using solutions of Ce^{3+} or Ti^{3+} instead of stannous chloride. 40

Example 7

Zeolite 13X was immersed in an aqueous solution of 30 g/l cupric chloride, left to soak in that solution to permit ion exchange to occur and was then separated from the remaining solution. The separated product was then immersed in fresh solution and the whole process repeated until it had been given five immersions. Analysis showed at that time that the catalyst contained from 5 to 6% copper based on the dry weight. The product was then washed with water and dried. It was then immersed in a solution of equal parts methanol and methylene dichloride providing about 0.5% Na_2PdCl_4 and 0.5% stannic chloride, both measured as metal. The product is dried at room temperature and is then heated at 150°C for 2 hours while exposed to the ambient atmosphere. 45 50

The resultant catalyst had high activities both in the smoke mixture test described in British Specification No. 2 014 376 and in the synthetic test mixture test described above. 55

The catalysts produced in any of the Examples can be used in a smoking product or filter thereof as described in British Specification 2 014 376.

CLAIMS

1. A catalyst comprising a support, copper chemically bonded to the support, and a minor amount of a redox couple for the copper. 60
2. A catalyst according to claim 1 in which the support is alumina or an aluminosilicate.
3. A catalyst according to claim 1 or claim 2 in which substantially all the copper is chemically bonded to the support and the support is substantially saturated chemically with copper. 65

4. A catalyst according to any preceding claim in which the redox couple comprises divalent palladium.
5. A catalyst according to any preceding claim comprising 1 to 10% copper and less than 20%, based on the weight of copper, of redox couple.
- 5 6. A catalyst according to any preceding claim including stannic ions as promoter. 5
7. A catalyst according to any preceding claim that has been activated by heating for half to 4 hours at 100° to 200°C.
8. A catalyst according to claim 5 comprising 2 to 7% by weight copper and 0.05 to 2% redox couple and in which the support is a zeolite.
- 10 9. A catalyst according to any preceding claim including lithium ions as promoter. 10
10. A catalyst according to any preceding claim that has been activated by heating for half to 4 hours at 100° to 200°C and by contact with water vapour at the end of the heating.
11. A catalyst according to any preceding claim comprising calcium ions as promoter.
12. A catalyst according to any of claims 6, 9 or 11 in which the weight of promoter,
- 15 measured as metal is 0.5 to 2.5 times the weight of redox couple, measured as metal. 15
13. A catalyst according to claim 12 in which the redox couple is provided as PdCl_2^- and any promoter is introduced as chloride.
14. A catalyst according to any of claims 1 to 13 in which the copper is mainly divalent but copper on the exposed surfaces is substantially monovalent and the catalyst is in the form of a
- 20 stable product. 20
15. A redox catalyst comprising copper chemically bonded to a support and in which the copper is mainly divalent but copper on the exposed surfaces is substantially monovalent and the catalyst is in the form of a stable product.
16. A catalyst according to claim 1 or claim 15 substantially as herein described with
- 25 reference to any of the Examples. 25
17. A process for making a catalyst according to any of claims 1 to 5 comprising forming a catalytic support to which copper is chemically bonded and then depositing a minor amount of a redox couple onto the support.
18. A process according to claim 17 in which the catalytic support to which copper is
- 30 chemically bonded is formed by impregnating this support with a solution of a cupric salt, 30
- permitting ion exchange to occur, removing excess solution and repeating the impregnation at least once and the deposition of redox couple is effected by impregnating the support carrying copper with a solution of the compound providing the redox couple and evaporating the solution to dryness and the catalyst is then activated by heating at 100° to 200°C for half to 4 hours.
- 35 19. A process according to claim 18 in which activation is improved by contacting the 35
- catalyst with water vapour at the end of the heating.
20. A process according to any of claims 17 to 19 in which a promoter selected from a compound of stannic, cupric, lithium or calcium is also deposited onto the support to which copper is bonded.
- 40 21. A process according to any of claims 17 to 20 in which the redox couple is palladium 40
- introduced as PdCl_2^- and any promoter is introduced as chloride.
22. A process according to claim 18 or claim 19 in which the heating is conducted for 1 to 3 hours at about 150°C.
23. A process according to claim 19 or claim 22 in which the heating is conducted under
- 45 vacuum in a closed vessel and then sufficient water is introduced to raise the pressure 45
- substantially to atmospheric.
24. A process of making a catalyst according to claim 14 or claim 15 from a support to which is bonded divalent copper, the process comprising converting copper on the exposed surfaces of the support to substantially monovalent copper.
- 50 25. A process according to claim 24 in which the conversion is conducted by heating the 50
- support carrying copper at 100 to 200°C for half to 4 hours and by contacting it with water vapour at the end of the heating.
26. A process according to claim 24 in which the conversion is conducted by contacting the
- 55 divalent copper with a reducing agent under conditions such as to form substantially monovalent copper. 55
27. A process according to claim 26 in which the reducing agent is selected from compounds of Sn^{2+} , Ti^{1+} and Ce^{3+} .
28. A catalyst made by a process according to any of claims 17 to 27.
29. A smoking product or a filter for a smoking product comprising a catalyst according to
- 60 any of claims 1 to 16 or 28. 60